AD A072855

DDC FILE COPY

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: 3	2. GOVT ACCESSION NO.
3. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle): The Kinetics of Hydrolytic Aging of Polyester Urethane Elastomers	5. TYPE OF REPORT & PERIOD COVERED: Technical; 9-78 to 8-79
	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s): D. W. Brown, R. E. Lowry, and L. E. Smith	8. CONTRACT OR GRANT NUMBER(s): NR 356-647
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Polymer Science and Standards Division, National Bureau of Standards, Gaithersburg, MD 20234	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS: Office of Naval Research, 800 N. Quincy St., Arlington, VA 22217	12. REPORT DATE: July, 1979
	13. NUMBER OF PAGES: 21
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report)
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

DDC RECEIVED AUG 17 1979 C

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

Submitted to Macromolecules.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Aging of polymers; degradation of polymers; hydrolytic stability; lifetime prediction; polyurethane; service life.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The hydrolytic degradation of polyester urethane elastomers is due to the acid catalyzed hydrolysis of the ester group. Acid content (A) and the reciprocal of the number average molecular weight (M^{-1}) increase by equivalent amounts indicating that each molecular chain scission produces one acid group. The time (t) dependence of A and M is given by:

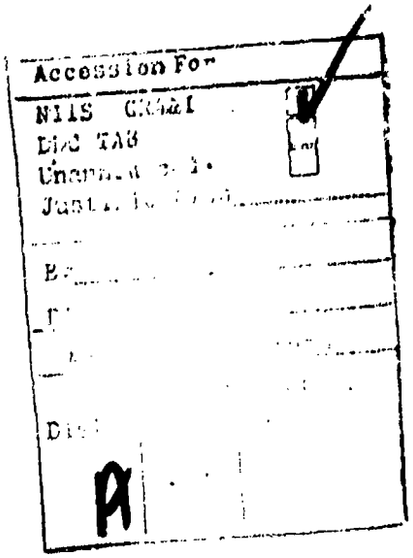
$$A = A_o e^{kt} \text{ and } M^{-1} = M_o^{-1} + A_o(e^{kt}-1)$$

(cont. on reverse)

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE S/N 0102-014-6601

BLOCK 20 ABSTRACT (cont.)

where the subscripts denote initial values. The fractional rate of increase in acidity, k, is a pseudo first order rate constant because the ester and water contents change only slightly with degradation. Values of k at 85°C and 100% relative humidity are in the range 15-20% per day for polyurethanes, based on polycaprolactone and polytetramethylene adipate diols. At 100% relative humidity k obeys the Arrhenius equation between 35 and 85°C with activation energies in the range 68-83 kJ/mol (16-20 kcal/mol). Values of k decrease with relative humidity, becoming zero in dry air.



AD A072855

THE KINETICS OF HYDROLYTIC ACING OF POLYESTER URETHANE ELASTOMERS

Daniel W. Brown, Robert E. Lowry, and Leslie E. Smith

Polymer Science and Standards Division
National Measurement Laboratory
National Bureau of Standards
Washington, D.C. 20234

DDC FILE COPY

79 08 16 037

Abstract

The hydrolytic degradation of polyester urethane elastomers is due to the acid catalyzed hydrolysis of the ester group. Acid content (A) and the reciprocal of the number average molecular weight (M^{-1}) increase by equivalent amounts indicating that each molecular chain scission produces one acid group. The time (t) dependence of A and M is given by :

$$A = A_o e^{kt} \text{ and } M^{-1} = M_o^{-1} + A_o(e^{kt}-1)$$

where the subscripts denote initial values. The fractional rate of increase in acidity, k, is a pseudo first order rate constant because the ester and water contents change only slightly with degradation. Values of k at 85°C and 100% relative humidity are in the range 15-20% per day for polyurethanes, based on polycaprolactone and polytetramethylene adipate diols. At 100% relative humidity k obeys the Arrhenius equation between 35 and 85°C with activation energies in the range 68-83 kJ/mol (16-20 kcal/mol). Values of k decrease with relative humidity, becoming zero in dry air.

Introduction

Polyester based urethane elastomers degrade in moist air, sometimes reverting to viscous liquids [1,2]. Lifetime prediction tests based on changes in physical properties can be misleading because of the reinforcing effect of crystals which form from degraded, lower molecular weight fragments [3]. More reliable tests based on specific molecular mechanisms are therefore desirable for critical uses of these materials. Schollenberger and Stewart showed that the degradation involved the acid catalyzed hydrolysis of the ester linkage [4]. They suggested that the degradation should be autocatalytic, since an acid group is expected to form for each ester group hydrolyzed. If the logarithms of the acid numbers that they report are plotted versus time reasonably linear behavior is found, consistent with their suggestion. This paper develops the kinetics of the degradation mechanism and presents a method to predict the lifetime of the polymers.

Experimental

Polyester and polyether based thermoplastic elastomers were obtained from three manufacturers. Qualitative analysis [5] showed that the polyester urethanes contained 1,4-butanediol, p,p' diphenylmethane diisocyanate, and either an adipate or caprolactone polyester. Infrared spectra showed no bands attributable to carbodiimides, which have been used to stabilize polyester urethanes to moisture [4]. Weight fractions of diisocyanate were calculated from the nitrogen contents, which were determined in duplicate by a commercial laboratory. Polytetramethylene adipate and polycaprolactone diols were obtained from commercial sources. Stabilized tetrahydrofuran was used as a solvent at 23-25°C for gel permeation chromatography and at 25°C for viscosity measurements on the commercial polyurethanes.

A hard segment polymer was made from diphenyl methane diisocyanate and butanediol (1:1 mol ratio) by the method of Lyman [6]. The polymer was in-

soluble in tetrahydrofuran but dissolved in dimethyl formamide, in which the intrinsic viscosity, [η], was 0.81 dℓ/g at 25°C.

A polyurethane potting compound which had reverted to a viscous liquid after 25 months service in a military aircraft was made available to us for this study. The compound contained 20% inorganic filler which was separated by dissolving the organic component and filtering.

The acid content, A, was measured by dissolving polymer containing 10^{-5}-5×10^{-4} equivalents of acid in 75 cm^3 of dimethyl formamide and titrating the solution with standard 0.02 N tetrabutyl ammonium hydroxide. This had been prepared from an ethanolic 1 M solution by dilution with methanol, isopropanol, and toluene (30:5:450 volume ratio); it was standardized against benzoic acid. A titration was run on the dimethyl formamide solvent and the titer was subtracted from that of the polymer solution. The titer of the blank was between 0.16 - 0.26 cm^3 provided that the dimethyl formamide had been stored over molecular sieve 4A, which had been heated previously in vacuum overnight at 170°C. Solvent titers became much larger if this drying agent was not used, probably because of the formation of formic acid [7]. The solutions were protected from atmospheric carbon dixoide during the titrations by prepurging with nitrogen and titrating into narrow-mouthed bottles. Titrations were generally done in duplicate and were reproducible to 1-2% and 10-20% at acid contents of 50-80 $\times 10^{-5}$ equivalent/g and 0.4-1.5 $\times 10^{-5}$ eq/g respectively. The chief difficulty in this method of determining A is that the yellow tint of the polymer solutions makes the end point imprecise when using a thymol blue indicator.

The number average molecular weights, M, were calculated from gel permeation chromatograms. A commercially available chromatograph with a septumless injector and a refractive index detector was used with a column set consisting of four microstyrogel-packed columns, one each of nominal pore sizes 10^2, 10^3, 10^4, and 10^5 Å. The solvent flow rate was 1 cm^3/min. A universal calibration ($M \cdot [\eta]$ as a function of retention volume [8]) was established using polystyrene

standards of narrow molecular weight distribution. Aged and unaged specimens of one of the polyurethanes were run through the chromatograph. A computer program and the universal calibration were used to calculate K in the Mark Houwink equation ($[\eta] = KM^a$) by using each chromatogram and the separately measured intrinsic viscosity, and assuming values of the exponent, a, equal to 0.5, 0.625, and 0.75. The arithmetic mean K for the set of polymers was calculated for each value of a, giving three Mark-Houwink equations for the set. The computer program was now used to calculate $[\eta]$ and M from each chromatogram for each Mark-Houwink equation. The set of data taken as correct was that for which $\Sigma(|[\eta]_c-[\eta]|/[\eta])$ was least, where $[\eta]_c$ and $[\eta]$ are computed and measured intrinsic viscosities respectively. The above sum divided by the number of polymer samples in the set was in the range 0.05-0.10, indicating an average 5-10% discrepancy between computed and measured intrinsic viscosities. The process was repeated for each polyurethane.

Samples were aged in sealed tubes in thermostated baths. Agings were done in dry air (over well-dried silica gel) and wet air at temperatures of 35, 44, 55, 70, and 85°C. At the three lower temperatures agings were also done in vacuum and in water vapor. Wet agings were done at 100% relative humidity (R.H.) except in a few of the runs at 55 and 85°C. At 55°C, 20% RH was maintained by keeping the water in the tube at 25°C (outside the 55°C bath). At 85°C, a lithium chloride solution was used to give 50% RH [9].

Gases above the samples were analyzed chromatographically after typical aging periods at each temperature. The oxygen-nitrogen ratio was almost the same as that in laboratory air, indicating that little oxidation had occurred.

Water contents at 100% RH were measured by soaking polymers in water for 24 hours in thermostatted baths. Samples were blotted, weighed in well stoppered tubes, pumped to dryness overnight, and reweighed. The procedure was repeated using 66 hour soaking and drying times to ensure that equilibration had occurred. For water contents at other humidities, samples were weighed after being kept for several days at the humidity specified.

Results

The intrinsic viscosities of the hard segment polymer and of three polyether urethanes did not change after wet or dry aging for 20 days at 85°C, 48 days at 70°C, 145 days at 55°C, or 341 days at 44 and 35°C. Consequently, these polymers were not studied further. However, the results obtained are pertinent to polyester polyurethanes since they indicate that hydrolysis of the urethane linkage is not appreciable.

Polyester polyurethanes did not decrease in intrinsic viscosity when aged in vacuum or in dry air in the time-temperature combinations mentioned above. Aging in wet air or in water vapor reduced the intrinsic viscosities by about the same amounts. Therefore water is the active agent and oxygen does not affect the hydrolysis. In a year at ambient conditions (approximately 24°C, 50% RH) the acid content of the polyurethanes increased by about 0.15×10^{-5} eq/g while M and [η] did not change by detectable amounts.

The initial properties of the three polyester polyurethanes and two polyester diols are listed in Table I. Polyester contents of the polyurethanes were calculated from the nitrogen content by assuming that diphenylmethane diisocyanate is the only source of nitrogen and that there are two diisocyanate residues per butanediol residue. These are common proportions in thermoplastic elastomers [1]. The ester content is 100 minus the sum of butanediol and diphenylmethane diisocyanate. The material code consists of the percentage ester followed by letters identifying the ester -PCL for polycaprolactone and PTMA for polytetramethylene adipate.

Figure 1 shows chromatograms of polymer 67 PCL after aging at 85°C and 100% R.H. A chromatogram of the solvent, also shown in Figure 1, is clear of peaks out to an elution volume of 40 cm^3. Solvent contaminant peaks occurred between 43 and 48 cm^3 but these do not interfere with the polymer peaks. Retention volumes of the polystyrene calibrants (molecular weight range 560-820000) are

marked along the top of the diagram. This calibration was approximated by the set: $\log(M\cdot[\eta])$, V; 6.34, 22.5; 2.95, 33.65; 1.07, 37.5. The computer program extrapolates linearly from the two nearest points if the volume is outside the calibration range. Also, it puts a linear baseline between chosen initial and final retention volumes. The initial and final volumes used were generally one cm^3 less and one cm^3 more than the appearance and disappearance of the polymer peaks.

The Mark Houwink relation found for polymer 67 PCL was:

$$[\eta] = 3.882 \times 10^{-3} M_v^{0.5}$$

where M_v is the viscosity average molecular weight. The numbers in Figure 1 under the aging periods are the number average molecular weights calculated by the computer routine. In Table II these M are listed along with observed intrinsic viscosities, calculated intrinsic viscosities, and acid contents. The agreement between observed and calculated intrinsic viscosities was worse at 85°C than at lower temperatures, probably because the range of $[\eta]$ was wider. The near equivalence of results with large and small pellets at 18.2 days indicates that diffusion of water is not rate limiting. Physical properties range from those of high modulus rubbers to those of soft materials that fail at slight extension. There is one set of chromatograms and tabulated data for each polymer at each temperature and each relative humidity. For economy of presentation these data will not be given.

It will be shown later that a comparison of interest is the time (t) dependence of the quantities $\ell n[(A_0 + M^{-1} - M_0^{-1})/A_0]$ and $\ell n(A/A_0)$, where subscript zeros indicate use of initial values. Figure 2 is a plot of these quantities versus time for agings of polymer 67 PCL at 85 and 70°C. Flagged symbols indicate use of molded sheets of initial intrinsic viscosity 0.8 dℓ/g. Apparently, molding did not affect the aging. Figure 3 is a similar plot of

results for this polymer at 35, 44, and 55°C.

The slopes of these lines will be interpreted as pseudo first order rate constants. Table III lists the slopes found for all polymers and diols that we studied. k_A is the slope of $\ln(A/A_0)$ vs. t and k_M is the slope of $\ln[(A_0 + M^{-1} - M_0^{-1})/A_0]$ versus t. The slopes were calculated by the method of least squares; the number after ± is the standard error. If no standard error is given, the k was calculated from only two values. The origin should be a valid point on all plots but was not used in calculating the slope if two other points were available. This was to avoid the effect of a large percentage error in A_0, which is small and may not be accurately known. Any error in A_0 does not affect k_A if the origin is not used. A_0 only affects k_M slightly provided that $\Delta(M^{-1})$ is much larger than A_0. Notice also that the effect of any error in M_0 on k_M becomes less important at severe degradation, since M^{-1} will be much greater than M_0^{-1}.

Degradation at 35°C, 100% RH and at 55°C, 20% RH was not great even after aging for about one year. Consequently, k_M and k_A probably are more uncertain than at other conditions, even though the standard error is not always a larger percentage of k_M. Since no degradation occurred in dry air k_M and k_A are regarded as equal to zero at 0% RH. At humidities between zero and 100% one can regard the k as being approximately proportional to the R.H. The diols were not aged at 35-55°C because they are solids at these temperatures. Only k_A of the diols was determined as their molecular weights are too low for changes to be measured with our column set.

Equilibrium water contents are plotted versus temperature in Figure 4. Values are accurate to about 0.1% water. They do not change appreciably during degradation. At 85°C the water content decreased with R.H. by a larger factor than did k_A.

The availability of the reverted potting compound permits comparison with a failure that occurred in actual use. The acid content of the organic com-

ponent of the potting compound was 1.6×10^{-3} eq/g. If the initial acid content was $1\text{-}2 \times 10^{-5}$ eq/g, typical of unaged polymers, then the average $10^2 k_A$ for 750 days is about 0.6 day^{-1}.

Discussion

Thermoplastic polyester urethane elastomers typically consist of "soft segment" polyester blocks with 10-20 ester links and a molecular weight of 1000-2000 that are joined by urethane linkage to "hard segment" blocks consisting of two MDI residues connected by a butanediol residue [1]. Scission of one ester linkage in the 10-20 in the soft segment will reduce the molecular weight of the polyurethane to values of about 1000-2000. Materials this low in molecular weight are not elastomeric. Consequently, severe degradation of mechanical properties can occur without an appreciable fraction of the ester groups being consumed.

Since the urethane linkage seems stable under the conditions studied, let us assume that the only reaction is the acid catalyzed hydrolysis of the ester linkage :

$$-- CO_2 -- + H_2O \xrightarrow[k]{A} -- OH + -- CO_2H$$

Each scission generates one acid group and one additional polymer molecule so that ΔM^{-1} equals ΔA. If the rate is first order in acid concentration :

$$\frac{d(M^{-1})}{dt} = \frac{dA}{dt} = kA$$

Here k, the fractional rate of increase in acid content, is a pseudo first order rate constant because the ester and water concentrations do not change appreciably over the extent of reaction studied. The equations give rates per gram of polymer which can be converted to a volume basis by multiplication by the density. Integration gives :

$$A = A_0 e^{kt} \qquad (1)$$

$$\frac{1}{M} = \frac{1}{M_0} + A_0(e^{kt}-1) \qquad (2)$$

Thus plots of $\ln(A/A_0)$ and $\ln[(A_0 + M^{-1} - M_0^{-1})/A_0]$ versus t should have the same slope, k. Figures 2 and 3 show such linear plots where the slopes from acid number and molecular weight determinations are seen to agree well, considering that A and M are arrived at by very different means. The uncertainty in A_0 is probably responsible for failure to go through the origin. Good agreement between k_A and k_M was also found for the other polymers as shown in Table III.

Taking k as the arithmetic mean of k_A and k_M, an Arrhenius plot is acceptably linear except for the result for polymer 67 PCL at 35°C as shown in Figure 5. The lines shown are from a least square analysis that does not include this point because its deviation from the applicable line is more than 10 times the average deviation. Table IV lists the k's at 85°C, 100% RH and their activation energies.

If the k for polymers are divided by the fraction of polyester one gets values normalized to a basis of 100% polyester, denominated as k' in Table IV. These agree reasonably well with values of k for the polyester diols alone indicating that the chemistry of the degradation is not affected by the presence of the hard segment.

The structures of polycaprolactone and polytetramethylene adipate esters are $[(CH_2)_4CO_2]_n$ and $[(CH_2)_4OC(CH_2)_4CO_2]_n$, respectively. As the structures are very similar it is not surprising that the k are also all rather comparable in size. We have no convincing explanation for the slightly higher activation energy of polymer 67 PCL.

Lifetimes, t_L, may be estimated by using values of k, M_0, and A_0, and substituting limiting values, A_L and M_L, for acid contents and molecular weights in equations 1 or 2, which may then be solved for t_L:

$$t_L = \frac{\ln(A_L/A_0)}{k} = \frac{\ln\left(\frac{A_0 + M_L^{-1} - M_0^{-1}}{A_0}\right)}{k} \qquad (3)$$

A_0 and M_0 may be taken from Table I. Tensile measurements for the three polymers after aging suggest that M_L and A_L are about 5000 g/mol and 1.6×10^{-4} eq/g respectively. At 35°C, 100% RH values of k from the lines of figure 5 are 0.18, 0.46, and 0.44×10^{-2} day^{-1} for polymers 67 PCL, 71 PCL, and 63 PTMA respectively. Values of t_L in Table IV were calculated using the above figures in equation 3. If the value of k for polymer 67 PCL is the value found experimentally, 0.11×10^{-2} day^{-1}, instead of that on the lowest line, then t_L would be about 2200 days. The exponential nature of equations 1 and 2 means that the degradation accelerates markedly with time. Consequently, the time interval between marginal usefulness and complete failure may be small. Lifetime estimates at varying temperatures and humidities should make use of a k that is appropriately weighted for the fraction of time spent in each condition.

The equations used here can be applied to lifetime estimates of filled insoluble polyester urethanes by degrading a series of samples at two or more high temperatures until the organic component is soluble at two different aging times at each temperature. After filtration, the acid content of the organic portion can be determined. The variation of A with time then gives k by equation (1), since the calculation can be done with the ratio of two acid contents and the aging time increment associated with them. The acid contents could be extrapolated backward in time to give A_0 for undegraded polymer and also an A characteristic of the limiting lifetime. This limiting lifetime probably would be judged by the physical behavior of samples degraded less extensively than those used for the acid measurements. Extrapolation of k by the Arrhenius equation would give values at the temperatures of interest. Lifetime estimates would involve use of equation (3) with values of k, A_0, and the A characteristic of the limiting lifetime.

Acknowledgements. The authors thank: Dr. Frank McCrackin and Walter J. Pummer of the National Bureau of Standards for devising the program used to calculate the molecular weights and preparing the hard segment polymer respectively, Dr. Charles S. Schollenberger of the B. F. Goodrich Co. for describing the method used in determining the acid contents, and Charles F. Bersch and John Cartowsky of the Naval Air Systems Command for providing the failed potting compound. The work was supported by the Office of Naval Research.

References

(1) P. Wright and A.P.C. Cumming, Solid Polyurethane Elastomers, Gordon and Breach, N.Y. 1969.

(2) C.F. Bersch, Naval Air Systems Command, Private communication.

(3) D.W. Brown, R.E. Lowry and L.E. Smith, Durability of Macromolecular Materials, ACS Symposium Series, 95, 145 (1979).

(4) C.S. Schollenberger and F.D. Stewart, J. Elastoplastics, 3, 28 (1971).

(5) R.L. Sandridge and R.F. Bargiband in Encyclopedia of Industrial Chemical Analysis, F.D. Snell and L.S. Ettre, Editors. Interscience, N.Y. 1974, 19, p. 262.

(6) D.J. Lyman, J. Polymer Sci. 45, 49 (1960).

(7) J.A. Riddick and W.B. Bunger, Organic Solvents, Wiley-Interscience, N.Y., 1970, p. 836.

(8) Z. Grubisic, P. Rempp, H. Benoit, J. Polymer Sci., B, 5, 753 (1967).

(9) E.U. Schuinder in Humidity and Moisture - Measurement and Control in Science and Industry. A. Wexler and W.H. Wildhack, Editors, Reinhold, N.Y., 1965, 3, 535.

Figure Legends

(1) Gel permeation chromatogram of polyurethane 67 PCL before and after aging at 85°C, 100% R.H. Aging period and corresponding value of M are indicated. Top scale, Universal Calibration Data.

(2) Polyurethane 67 PCL pellets. Full symbols, $\ln(A/A_0)$ vs. t; open symbols, $\ln[(A_0 + M^{-1} - M_0^{-1})/A_0]$ vs. t. 100% RH: 85°C ●, ○; 70°C ▲, △. 50% RH, 85°C ■. Flagged symbols, pressed strips.

(3) Polyurethane 67 PCL. Filled symbols, $\ln(A/A_0)$ vs. t; open symbols, $\ln[(A_0 + M^{-1} - M_0^{-1})/A_0]$ vs. t. 100% RH: 55°C ●, ○; 44°C ■, □; 35°C ▲, △. 20% RH, 55°C ▽.

(4) Weight % water vs. temperature. 100% R.H.: X, 67 PCL; ○, 71 PCL; ●, 63 PTMA. 50% RH Flags above same symbols. 20% RH Flags below symbols.

(5) Arrhenius plot of k at 100% RH. ○, 67 PCL; △, 71 PCL; □, 63 PTMA; ●, 100 PCL; ■, 100 PTMA.

Table I

Properties of Unaged Polyester Diols and Polyester Polyurethanes

Material	Ester Wt %	Form	[η] dℓ/g	10^{-4}M g/mol	10^{5}A eq/g
67 PCL	67	Ellipsoid[1]	1.50	2.66	1.4
71 PCL	71	Sheet[2]	0.98	2.25	0.38
100 PCL	100	Wax	----	0.123[3]	0.36
63 PTMA	63	Flake[4]	0.81	1.81	1.05
100 PTMA	100	Wax	----	0.200[3]	2.09

[1]Range of minor diameters 1-4 mm

[2]0.25 mm thick

[3]From hydroxyl content

[4]Thickness range 0.5-2 mm

Table II

Degradation of Polymer 67 PCL at 85°C, 100% RH in Wet Air

Time	[η]	[η] calc	10^{-4} M	10^{5} A
Days	dℓ/g	dℓ/g	g/mol	eq/g
0	1.5	1.50	2.66	1.55
3.7	1.35	1.34	2.45	1.78
12.0	0.64	0.676	1.12	5.33
18.2[a]	0.32	0.382	0.484	14.4
18.2[b]	0.33	0.395	0.528	
22.3	0.21	0.281	0.280	31.4
28.3	0.13	0.193	0.104	82.5

a) Single pellet, weight 0.0528 g

b) 21 pellets, total weight 0.0544 g. The chromatogram of this sample is not shown in Figure 1 because it is nearly identical to that of the other 18.2 day sample.

Table III

Rate Constants, k_M and k_A, at Various Temperatures

100% RH except as indicated

Material	Rate Constant	35°C	44°C	55°C	70°C	85°C
	10^2 Day^{-1}					
67 PCL[1]	k_M	0.10±0.04	0.47±0.04	1.53±0.16	4.9±0.5	15.7±0.4
	k_A	0.12	0.37	1.2	4.5±0.1	15.8±0.8
71 PCL[2]	k_M	0.34±0.08	1.6	2.5 ±0.3	5.5±0.6	18.3±2.0
	k_A	0.47	0.8	2.0 ±0.2	8.1±0.2	19.7±0.9
100 PCL	k_A				10.5±0.4	29 ±3
63 PTMA[3]	k_M	0.41± 0.05	1.04±0.04	2.5 ±0.2	6.7±0.6	19.7±1.6
	k_A	0.47	0.95	2.6 ±0.1	8.0±0.1	20.4±0.5
100 PTMA	k_A				10.4±0.3	30.3±0.5

1) At 20% RH, 55°C, $10^2 k_M \sim 0.1$ Day^{-1} and at 50% RH, 85°C, $10^2 k_A = 6.9 \pm 0.3$ Day^{-1}

2) At 20% RH, 55°C, $10^2 k_M \sim 0.3$ Day^{-1}

3) At 20% Rh, 55°C, $10^2 k_M \sim 0.3$ Day^{-1} and at 50% RH, 85°C, $10^2 k_A = 9.77 \pm 0.04$ Day^{-1}

Table IV

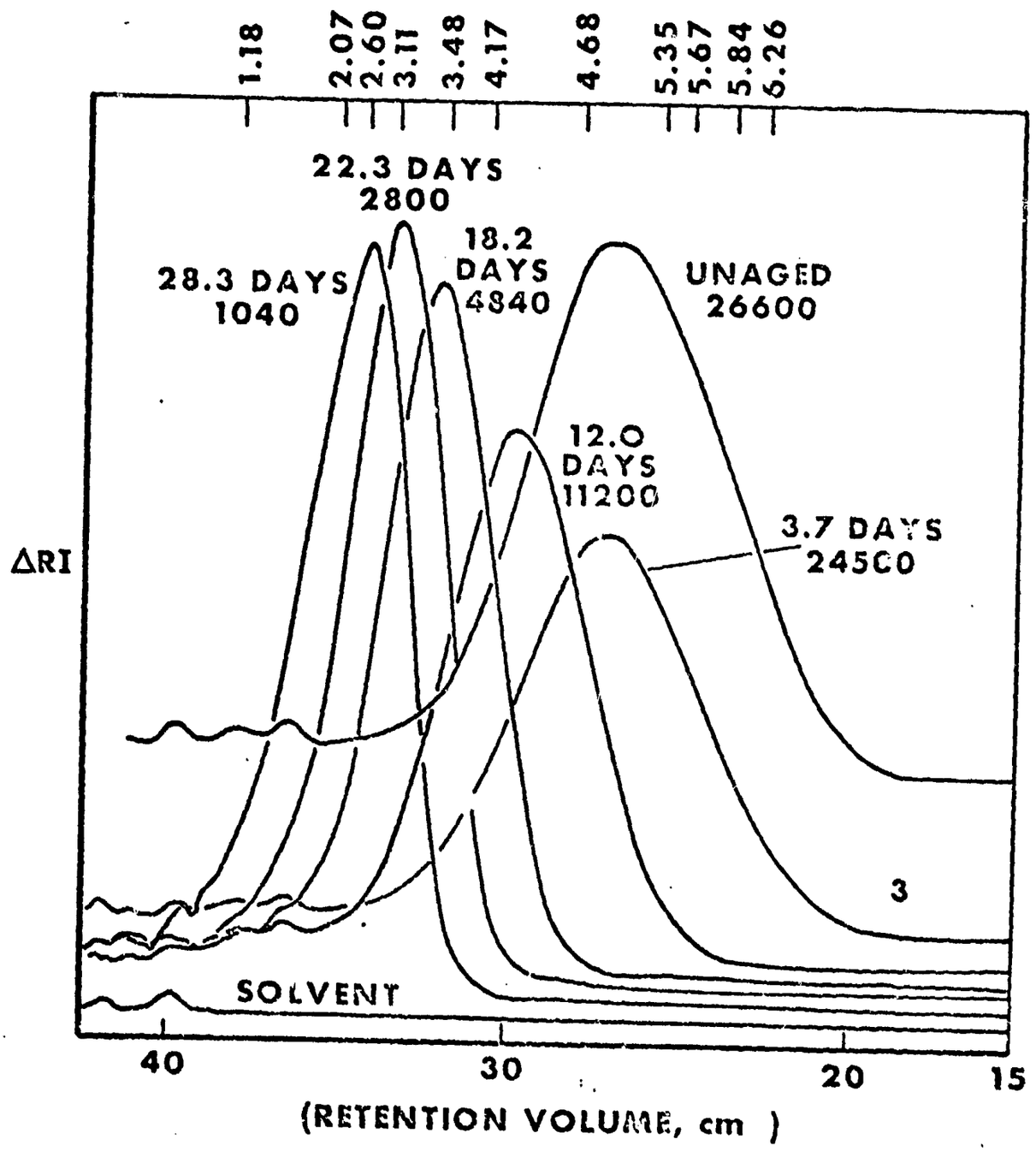
Rate Constants at 85°C, Activation Energy, and Lifetime at 35°C RH 100% for all

Material	10^2 k day^{-1}	10^2 k′ day^{-1}	E KJ/mol[1]	t_L days
67 PCL	16	24	83.3±2.1	1400
71 PCL	19	27	68.0±3.1	800
100 PCL	29	29	69.5	
63 PTMA	20	32	69.8±1.0	600
100 PTMA	30	30	72.8	

(1) 1 kJ = 0.239 kcal

Fig 1

GPC OF POLYURETHANE 67 PCL AGED AT 85 °C; 100% RH



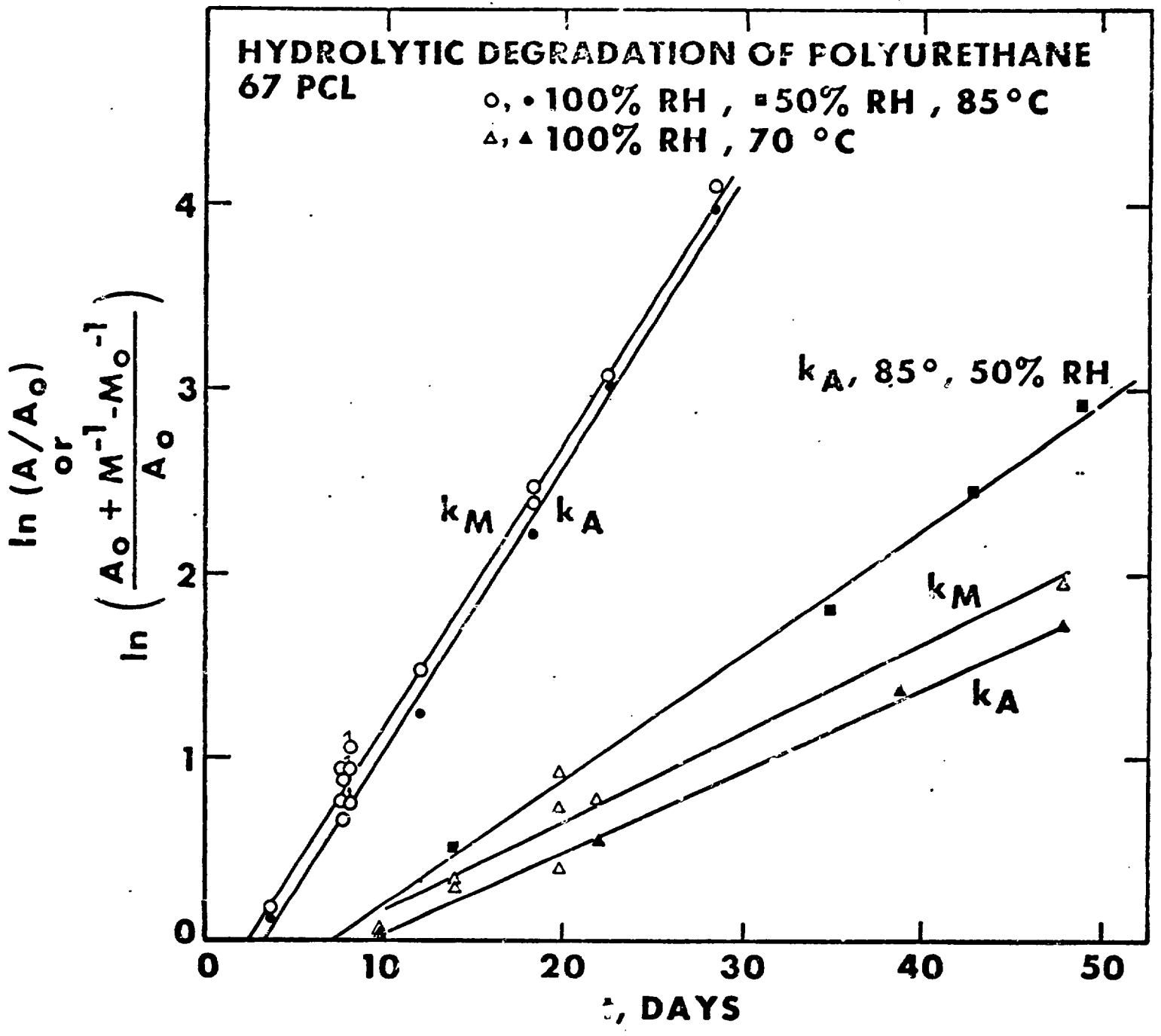

HYDROLYTIC DEGRADATION OF POLYURETHANE
67 PCL
○, • 100% RH , ▪ 50% RH , 85°C
△, ▲ 100% RH , 70 °C
k_A, 85°, 50% RH
k_M
k_A
k_M
k_A
$\ln (A/A_o)$ or $\ln\left(\frac{A_o + M^{-1} - M_o^{-1}}{A_o}\right)$
0
1
2
3
4
0
10
20
30
40
50
t, DAYS

Fig 2

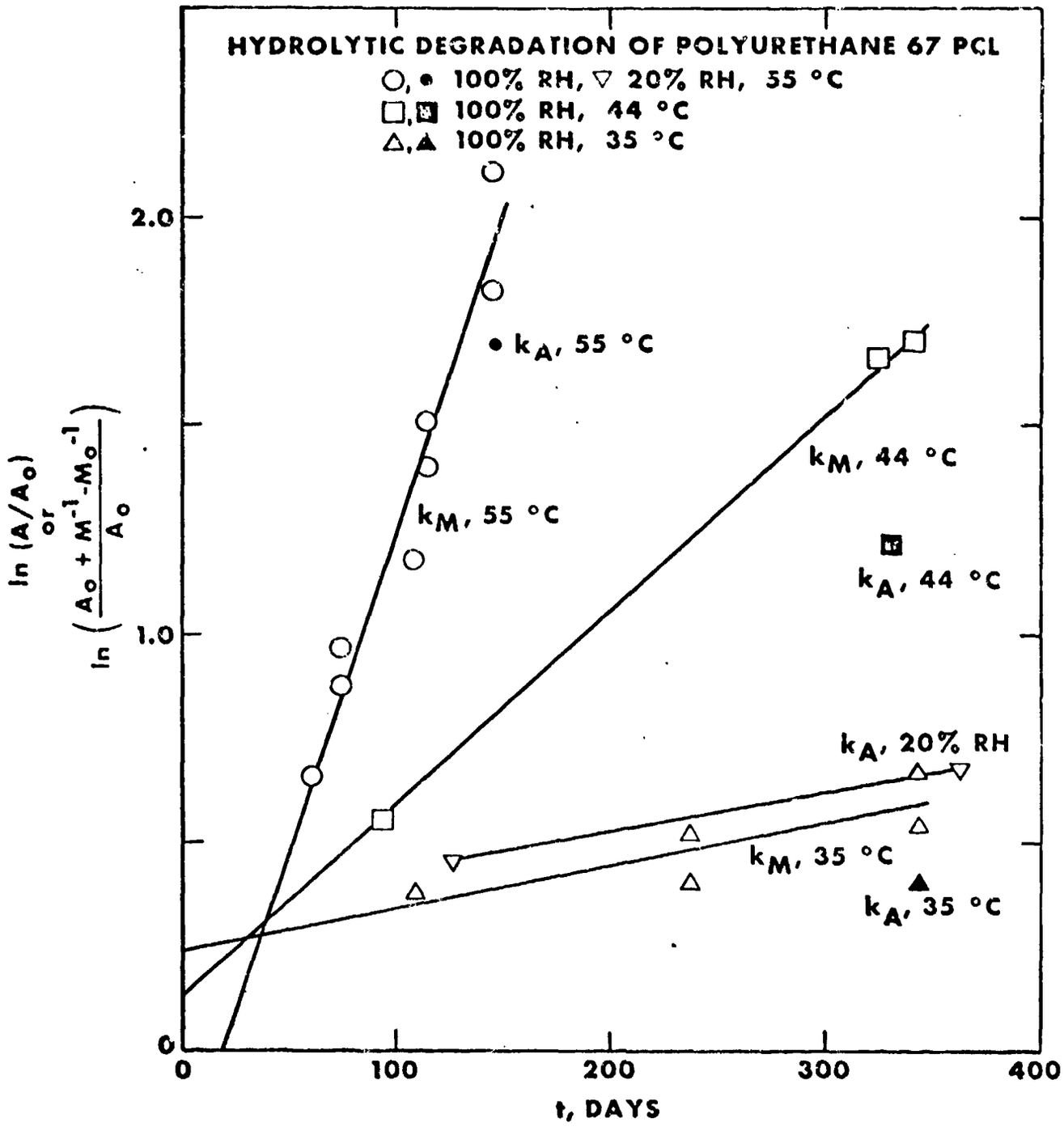

HYDROLYTIC DEGRADATION OF POLYURETHANE 67 PCL
○, ● 100% RH, ▽ 20% RH, 55 °C
□, ■ 100% RH, 44 °C
△, ▲ 100% RH, 35 °C
k_A, 55 °C
k_M, 55 °C
k_M, 44 °C
k_A, 44 °C
k_A, 20% RH
k_M, 35 °C
k_A, 35 °C
$\ln (A/A_o)$ or $\ln\left(\frac{A_o + M^{-1} - M_o^{-1}}{A_o}\right)$
2.0
1.0
0
0
100
200
300
400
t, DAYS

Fig 3

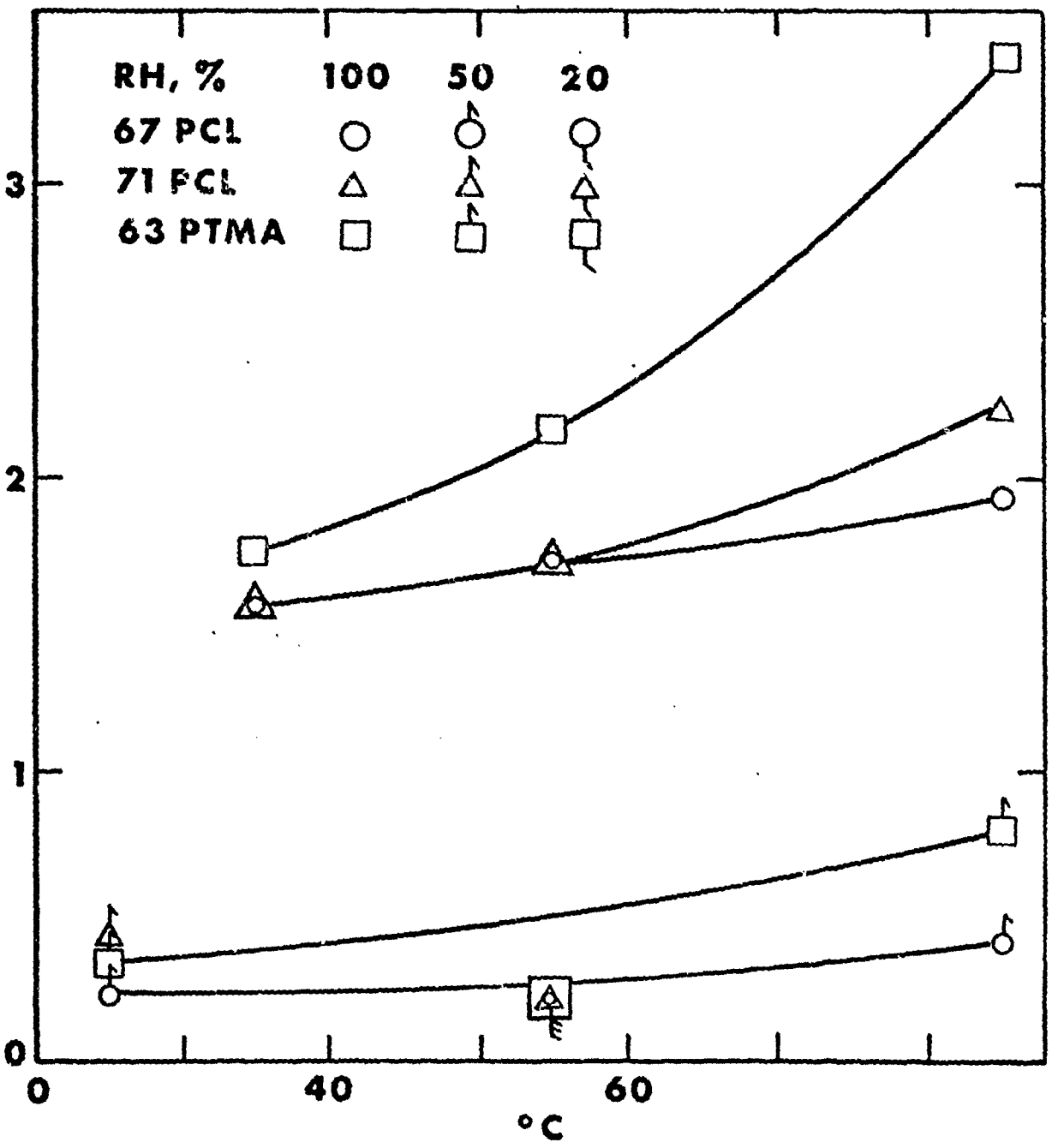


Fig 4

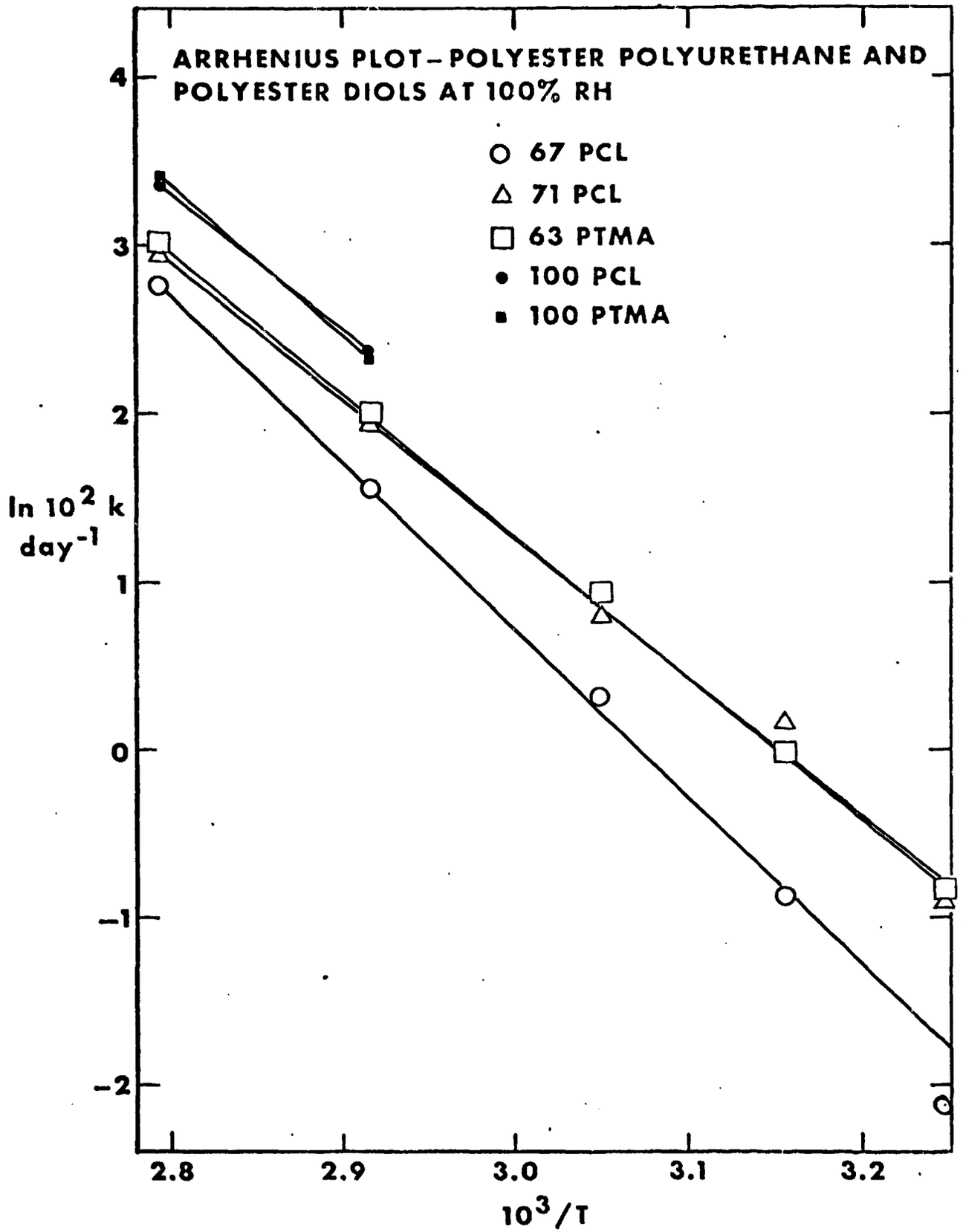

ARRHENIUS PLOT–POLYESTER POLYURETHANE AND POLYESTER DIOLS AT 100% RH
67 PCL
71 PCL
63 PTMA
100 PCL
100 PTMA
ln 10² k day⁻¹
4
3
2
1
0
−1
−2
2.8
2.9
3.0
3.1
3.2
10³/T

Fig 5